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Vibrational Spectroscopy Study of the Chemistry of Trimethylamine on Pt(111)

by

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Submitted to Surface Science

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ABSTRACT

Trimethylamine ($(CH_3)_3N$) is an important reagent for characterization of surface acidity and many industrial catalytic reactions. This report is the first attempt to characterize trimethylamine on Pt(111) surface using TPD and HREELS. From TPD, it is found that only H_2, HCN and $(CH_3)_3N$ desorb from the surface. $(CH_3)_3N$ desorbs as a single peak at 250°C. The vibrational spectra at low temperature indicate that the molecule is weakly bonded to the surface through the nitrogen lone pair. Surface adsorbate species at different temperatures are identified with HREELS. Spectral changes at different sample temperature coincide with TDS spectra. CO and trimethylamine coadsorption experiments are also performed, which enables us to conclude that trimethylamine is adsorbed on top site. In addition, it is found that CO stretching frequencies are shifted as much as 40 cm^{-1} due to strong coadsorbates interaction. A possible reaction mechanism is proposed.

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Abstract

Trimethylamine ($(CH_3)_3N$) is an important reagent for characterization of surface acidity and many industrial catalytic reactions. This report is the first attempt to characterize trimethylamine on Pt(111) surface using TPD and HREELS. From TPD, it is found that only H_2, HCN and $(CH_3)_3N$ desorb from the surface. $(CH_3)_3N$ desorbs as a single peak at 250°C. The vibrational spectra at low temperature indicate that the molecule is weakly bonded to the surface through the nitrogen lone pair. Surface adsorbate species at different temperatures are identified with HREELS. Spectral changes at different sample temperature coincide with TDS spectra. CO and trimethylamine coadsorption experiments are also performed, which enables us to conclude that trimethylamine is adsorbed on top site. In addition, it is found that CO stretching frequencies are shifted as much as 40 cm^{-1} due to strong coadsorbates interaction. A possible reaction mechanism is proposed.

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1. Introduction

The surface chemistry of organonitrogen compounds on transition metals are of great interest because of many industrial applications, such as metal corrosion inhibitors and selectivity poisoner in catalysis. In this paper, trimethylamine surface chemistry on Pt (111) was studied using standard TDS and HREELS techniques.

There have been little studies on the adsorption of amine on clean, well characterized, transition metal surfaces. Baca, Schulz and Shirley[1] have studied methylamine on Ni and Cr surfaces at room temperature. The methylamine was found to adsorb on these metal surface molecularly with bonding through the nitrogen lone pair. Large intensity fluctuations of C-N stretch mode among these surface was observed, which was attributed to the variation of the angle between the surface normal and C-N bond. The decomposition of methylamine on Pt (111) surface has not been firmly established. One study[2] indicates that methylamine decompose upon heating to 300K with C_2N_2, H_2 and HCN as major desorption species, while other study[3] suggests that methylamine desorbs molecularly. Alkylamine on W surface has investigated by Pearlstine and Friend[4]. $(CH_3)_3N$ undergo complete irreversible decomposition for exposures lower than 0.25L. Thermal reaction of $(CH_3)_3N$ on W (100) results in desorption $(CH_3)_3N$, CH_4, H_2 and N_2. Walker and Stair[5] studied $(CH_3)_3N$ on clean and oxidized Mo(100). On clean Mo, $(CH_3)_3N$ initially decomposes to atomic species. after the surface has been partially passivated by these decomposition products, the adsorption of $(CH_3)_3N$ is molecular. The molecular adsorbate decomposes to produce CH_4, H_2, N_2 and HCN. This is in direct contrast the surface reaction of W surface where no HCN is observed.

To our knowledge, there have been no reported HREELS study of trimethylamine on well defined metal surfaces. In a sense, trimethylamine is a simple molecule. There are only two kinds bonds in the molecule, namely, C-H and C-N. This simplicity should provide us an ideal system to study surface chemistry of amine molecules.

In addition we studied CO and trimethylamine coadsorption on the Pt(111) surface. This study is inspired by the work of Queau and Poilblanc[6], and Sheets and Blyholder.[7] Queau and Poilblanc[6] studied CO and $(CH_3)_3N$ coadsorption on a evaporated Pt film. They found that upon adsorption of trimethylamine, the CO stretch frequency was lowered

by as much as 30 cm^{-1}. This coadsorption of CO and trimethylamine is studied again by Sheets and Blyholder[7] on iron and nickel films. .The results are very intriguing. When CO is added to trimethylamine preadsorbed iron or nickel film, the IR spectra resembles that of chemsorbed mono-methylamine. However, when trimethylamine is added to CO preadsorbed iron and nickel film, the IR spectra resembles that of chemisorbed dimethylamine. This large CO coadsorption effect was rationalized in terms of a molecular-orbital model.[8] In this model, the chemisorbed CO can accept electrons from the surface. When CO is coadsorbed with $(CH_3)_3N$, the electron-withdrawing CO results in the metal atom to which the is the nitrogen is coordinated becoming more positive, which in term promote methyl migration to positive centers. This model does provide explanation for the enhanced reactivity by CO. However, the reactivity dependence on the order of CO adsorption remains a mystery. From our more accurate measurements, we might arrive a better understanding of the adsorbates interaction.

2. Experimental

Experiments are performed in a conventional two-level UHV chamber. Auger electron spectrometer, LEED, quadrupole mass spectrometer and ion gun are mounted on the first level and HREELS on the second level. The base pressure of the chamber is $1x10^{-10}$ torr. The Pt (111) crystal is a disc of 1 cm in diameter which is oriented within 0.5 degree of (111) plane. Standard cleaning procedures, namely, Ar^+ ion bombardment and heating in oxygen, are applied to achieve clean surface. The cleanness is checked with AES. Auger spectroscopy is also used to determine relative trimethylamine surface coverages.

In this study, main techniques employed are HREELS and TDS. TDS has been a widely used simple surface chemistry technique for measurement of bond energy of adsorbates and the evolution of species. As pointed out by Riviere[9], there are several artefacts one needs aware when interpreting the TDS data. The most important of these is the desorption of gas from surfaces other than the desired one. In order to eliminate or minimize these artefacts, we developed a subtraction technique. Basically, after a normal TDS spectra is finished, a second TDS is taken with identical settings as the first TDS, except that the Pt crystal is facing away from the doser when dosing. This second TDS becomes a background of the first TDS. With this subtraction, the desorption peaks from the sample arms are eliminated, leaving clean thermal desorption spectra. The actual TDS

is done with the crystal heated resistively to 1000K and the quadrupole mass spectrometer multiplexed to sample 12 masses simultaneously. The heating rate is set at 5 K per second. The HREEL spectrometer (LK technology Inc.) consists of two 127-degree cylindrical deflectors as incident electron beam monochrometer and a rotatable single 127-degree cylindrical deflector as electron energy analyzer. On a clean surface, spectral resolution of 35 cm^{-1} at FWHM is readily achievable with a counting rate about ~10^5 counts/sec . Each digitized scan has a step size of 5 cm^{-1} carried out from -200 cm^{-1} to 3600 cm^{-1}. In some cases the scan ranges is increased to 4500 cm^{-1}, in order to make sure that NH_x species could be detected if they are formed.

Trimethylamine is supplied by Aldrich with a purity of 99%. It is used without further purification. The trimethylamine or CO is dosed onto the Pt surface with a direct doser. All the dosing was done while Pt sample is hold at -110 °C. The coverage is controlled by the time the Pt sample is facing the doser at a specific pressure increase ($5.0x10^{-10}$torr) in the vacuum chamber when the doser is on. With this method, the coverage can be easily reproduced.

3. Results and discussions

3.1 Thermal desorption of trimethylamine

Trimethylamine was adsorbed on a clean Pt(111) surface at about -110 °C. The desorption products were monitored with m/e = 2, 15, 16, 17, 18, 26, 27, 28, 30, 41, 43 and 58. Only hydrogen, hydrogen cyanide and trimethylamine are detected as desorption products. Methane, ammonia, acetalyne, nitrogen, ethane and acetonitrile were looked for but not found. Fig 1 shows a typical thermal desorption profile of trimethylamine adsorbed on the Pt(111) at -110 °C. $(CH_3)_3N$ desorbs molecularly at -50 °C. H_2 has two desorption peaks at 20 and 100 °C and HCN desorbs as a single peak at 250 °C. A carbonacceous residue remained on the surface after the TPD experiment. This residue was detected by Auger spectra, which is discussed later.

It is interesting to compare these results with the results obtained by Friend et al[4] and Stair et al[5], as summarized in Table 1. For those species observed, the desorption temperatures are similar. However, there is a major difference in which species are desorbed. On the Mo surface, the desorbing species are CH_4, HCN, and N_2. On the W

surface, the desorbing species are H_2, CH_4, N_2 and $(CH_3)_3N$. Pt surface is sort of in between the W and Mo surfaces, where the desorbing species are H_2, CH_4, N_2 and $(CH_3)_3N$.

From these TPD data, the sequen e of reaction of $(CH_3)_3N$ on Pt(111) become obvious. First, trimethylamine desorb molecularly from the surface at -50 °C. Further heating induces trimethylamine decomposition to produce H_2 at 30 and 150 °C. The presence of two H_2 desorption peaks suggests that they are formed from different surface species. At 250 °C, HCN desorbes from the surface.

3.2 Trimethylamine uptake with AES spectra

Fig 2 shows the carbon(272eV) / platinum(237eV) Auger ratio as a function of trimethylamine dosage. The solid and open diamonds are two separate experiments. The data is quite scattered. The cause is not clear. Maybe that electron induced desorption is occurring here. Because of this, saturation coverage was not determined. The solid triangle is due to auger signal taken after TDS. So it is quite clear that a lot of carbon has left the surface. Also to notice that the surface carbon concentration is sort of constant after TDS. This is another indication that multilayer trimethylamine are weakly bonded, as the temperature is increased to -50 °C, most of the trimethylamine already left the surface. Since in the TDS, the carbon are left as HCN, so we should have 2 carbon left on the surface for each decomposed trimethylamine molecules.

Fig 3 shows the carbon(272eV) / platinum(237eV) Auger ratio as a function of temperature at two different initial trimethylamine dosage. First to notice is that even at different dosage, the initial concentration of surface carbon revealed by AES is about the same, namely 0.8 In addition, we did not see carbon signal drop near -50 °C, as otherwise expected for the desorption of parent molecule. This is probably due to the electron induced desorption. Remember that the multilayer is weakly adsorbed on the surface. Secondly, the carbon signal drops at 200 °C. which coincide with the TDS data. In TDS, HCN starts to desorb at 200 °C and peaks at 250 °C.

If one plot C and N signal as a function of dosing time, One would expect that C signal should rise three times faster than that of N. Unfortunately, the Auger spectra, which simultaneously monitoring the C and N, were not taken in the present experiment.

3.3 HREELS of trimethylamine

Figure 4 shows the HREEL spectra of trimethylamine at low temperature. Considering this is quite a large molecule, it is quite surprising that many loss peaks are strong and well separated. In order to assign these spectra, one needs to understand the vibrational spectra of trimethylamine in gas phase, which has been investigated by several researchers[10]. In gas phase, a trimethylamine molecule has 22 vibrational modes. These modes and their frequencies are listed in Table 2. Since our HREELS spectra has resolution of about 40 wavenumber, we clearly cannot resolve all these peaks. We can lump together those peaks that are close to each other. so that we have

1. C---H stretch at about 2900 cm^{-1} ;
2. methyl deformation at 1440 cm^{-1}
3. methyl rock at 1270 and 1100 cm^{-1}
4. mehtyl wag at 1180 cm^{-1}
5. NC_3 asymmetric stretch at 1000 cm^{-1}
6. NC_3 symmetric stretch at 800 cm^{-1}
7. NC_3 deformation at 400 cm^{-1}

as shown in the Table 2. In this way the vibrational modes of trimethylamine molecules are reduced from 22 to about 7. This will make the assignment much easier. The adsorption of trimethylamine molecule on the Pt surface should give rise additional vibrational modes, such as Pt --$(CH_3)_3N$ stretch and NC_3 deformation modes. The frequencies of these modes can be estimated from the IR spectra of organometallic Pt and trimethylamine complexes. Combined with these information, following assignments are made:

1. C---H mode is easily identified, which is located around 2900 wavenumbers. difference in peak maximum between on and off spectra is expected. There are 6 C--H stretch modes, some of them are dipole active and some are not. The on-specular spectrum strongly enhance dipole scattering loss peaks,.while off-specular emphasis impact scattering. Also to notice that C---H mode loss peak is quite broad, suggesting that it is a superposition of many peaks. Because of these many modes are involved, we do not expect significant intensity change as we move the detector off-specular.

2. 804 wavenumber can be readily assigned to NC_3 symmetric stretch. This peak should be strongly dipole active. This is confirmed by the big intensity drop in the off-specular spectrum.

3. 1442 cm^{-1} can be assigned to methyl deformation. Again there are 6 deformation modes congested together, we are not expect to see intensity drop in the off-specular spectrum, as demonstrated in the spectra. Again, we notice the peak maximum

4. The 940 cm^{-1} can be assigned to NC_3 asymmetric stretch for the following reasons: a. In $PtCl_2(TMA_2)$, this mode lies in 970 cm^{-1} , which is quite close to 940 cm^{-1} . b. This peak is not strongly dipole active. c. As we raise the sample temperature, this peak diminishes in the same rate as the NC_3 symmetric stretch loss peak.

5. the methyl wag mode can be assigned to 1218 cm^{-1} and two methyl rocking mode can be readily assigned.to 1072 and 1250 cm^{-1} . Because the methyl is away from surface, these modes are less perturbed from their gas phase values.

6. the 511cm^{-1} peak is assigned to Pt ---N stretch because in $PtCl_2(TMA_2)$, this mode lies in 556 cm^{-1} and it is strongly dipole active.

7.The two small peaks at 312 and 390 cm^{-1} can be tentatively assigned to NC_3 symmetric and asymmetric deformation.

8.The 200 cm^{-1} might be NC_3 rocking mode. However, it is puzzling that it is strongly dipole active.

Figure 5 is HREELS of trimethylamine as a function of coverage. The overall spectral pattern does not change as the coverage is increased. There are two special feature needs to be addressed: First the intensity of C-N stretch(807cm^{-1}) seems to grow (relative the 947 cm^{-1} loss peak) as the trimethylamine coverage increases. At first sight, it looks strange because these loss peaks should rise or fall simultaneously. However this phenomenon can be easily explained with the model proposed by Shirley et al.[1] At low coverage, the trimethylamine adsorb on the pt (111) surface through the nitrogen lone pare. N-C bond is at a angle, θ, which is close to the gas phase value. The intensity is determined by the dynamical dipole moment on the surface, which is proportional to $\sin^2\theta$. As the coverage increases, the repulsion between the methyl group become more and more significant. This repulsion pushes the N-C bond closer to the surface normal, which consequently increases the dynamical dipole moment for this vibrational mode. Secondly, there is a broad band around 2200 cm^{-1} . This peak is normal attributed to CN stretching mode. The presence of the CN group suggesting that the initial trimethylamine adsorption is dissociative.

Figure 6 shows HREELS as a function of temperature on specular at a dosage of 300 secs Between -110 ^{o}C and -30 ^{o}C, we are not expect to see much change except some

intensity variation because from the TDS , the parent trimethylamine desorbs around -50 ^{o}C. compare the -100 ^{o}C and -30 ^{o}C spectra, we can see intensity drop due to parent molecule desorption. The desorption of hydrogen starts at 0 ^{o}C and peaks at 30 ^{o}C. Bigger spectral changes are expected for spectra taken above the 0 ^{o}C. From the 18 ^{o}C spectrum, following changes are noticed: First the growth of the 560 cm^{-1} peak, indicating new species are formed on the Pt(111) surface. Secondly the loss of 800 cm^{-1} and 960 cm^{-1} peaks, indication the decomposition the parent molecules.

As the temperature is increased to 55 ^{o}C the 800 and 960 cm^{-1}peaks are totally disappeared, suggesting the parent molecules are now completed decomposed. Accompany this loss is the strong growth of the 560 cm^{-1}. This 560 loss peak is stable up to 88 ^{o}C and disappear only after heating the sample to 116 ^{o}C. So what ever this new species is, it is quite stable on the Pt(111) surface.

In order to understand the what this new species is, off-specular HREELS spectrum was taken and it is shown in Figure 7. First to notice is that the 560 cm^{-1} loss peak is strongly dipole active. Secondly, we find that C---H loss peak is still present and the width is a lot narrower. Since the loss peaks at 1115, 1378 and 1495 cm^{-1} are normally associated with the methyl group, the new species must have methyl group attached to it. Thirdly, there is another dipole active mode, namely 1778 cm^{-1} loss peak. This frequency range is associated with some sort of double bonds, such as C==C or C==N. Since this loss peak is strongly dipole active, this double bonded species might be lie perpendicular to the surface normal. Based on this information, methyl iso-cyanide type surface species was proposed. Fortunately, methyl iso-cyanide on Pt(111) surface has been investigated by Avery and Matheson.[11] Comparison of HREELS spectra of methyl iso-cyanide with Fig. 7 is quite discouraging. Overall spectra patterns are quite different, indicating that the surface species is not methyl iso-cyanide type.

However, it is well known that methyl iso-cyanide can readily undergo isomerization to yield acetonitrile. As matter of fact, from their TPD spectra, Avery and Matheson concluded that acetonitrile is desorbed as one of the desorbing species, not methyl iso-cyanide. Since the $(CH_3)_3N$/Pt(111) sample has been heated to 40 ^{o}C, it is reasonable to assume that the intermediate methyl iso-cyanide type surface species can quickly convert to acetonitrile type surface species. Acetonitrile on Pt(111) was studied again by Avery et al.[12] Except some minor frequency differences, overall spectral

similarity between CH_3CN/Pt(111) and $(CH_3)_3N$/Pt(111) at 40 ^oC is astonishing. Therefore the spectra shown in Fig 7 is assign to CH_3CN/Pt(111) with assignment listed in Table 3

3.4 Coadsorption of CO and Trimethylamine on Pt(111) surface

In the previous discussion, we have made an assumption that N is bonded on the top on the Pt (111) surface. Can we find a way to probe the where the trimethylamine is adsorbed? Yes, there is a way and it is quite simple. we know that on a clean pt surface, CO molecule wants to adsorb on top site first. After the top sites are all taken, additional CO will that the bridge sites. The top site CO has a characteristic stretching frequency of 2070 cm^{-1} and the bridge site CO has a characteristic stretching frequency of 1820 cm^{-1}. If our assumption is true, namely trimethylamine is adsorbed on the top site, then a coadsorption experiment with methylamine adsorbed on a CO predosed pt surface , we should be able to block trimethylamine surface reaction

Figure 8 shows the CO and trimethylamine coadsorption HREELS spectra. The CO is dosed first to take over all the top sites. A little access CO is occupied on the bridge site. As we add trimethylamine onto the surface, a couple of dramatic spectral changes are noticed even at a temperature as low as -110 ^oC: first, CO stretching frequencies are being shifted to a lower values. The top site CO stretching frequencies are lowered from 2070 cm^{-1} to 2031 cm^{-1}. The bridge site CO stretching frequencies are lowered from 1822 cm^{-1} to 1788 cm^{-1}. Secondly, trimethylamine HREELS spectra stays the same, unaffected by the presence of CO.

As the sample temperature is increased, CO stretching frequency is shifted back to their original values, indicating trimethylamine are driven off from the surface. The important thing is that the loss peak at 560 cm^{-1} did not show up. Suggesting that the trimethylamine decomposition pathway has been blocked by CO, as we anticipated.

We can interpret the data as the following: CO are strongly bonded to the pt surface at top site. The incoming trimethylamine has to occupy bridge or triple sites, because the trimethylamine are only weakly bonded to the metal surface. Because the bulkiness of the trimethylamine molecule, the top-sited CO are pushed off their perpendicular positions,

leading the strong intensity loss. The dipole-dipole interaction between CO and trimethylamine may cause the shift of the CO stretching frequencies. As the sample temperature is increased, the trimethylamine is leaving the surface, the CO stretching frequency is restored.

If our hypothesis is true, we should see the trimethylamine decomposition reaction should occur if the trimethylamine is dosed before the CO dosage. Figure 9 shows the HREELS spectra of CO and trimethylamine coadsorption with trimethylamine dosed first. The bottom picture shows the normal trimethylamine on clean pt surface. The top spectrum is when CO is added. The first thing to notice is that the CO shows up at 1715 and 1607 cm^{-1}. This means that CO is not strong enough to push aside the trimethylamine. So they are occupying the bridge and hollow sites. Another big change when CO is added is the growing of broad peak at 2182 cm^{-1}. This frequency range is associated with the CN stretching mode. Again this demonstrate that the initial adsorption of trimethylamine on pt is dissociative. The addition of CO might cause the surface CN to stand up, thus increasing the peak intensity.The rest of the spectrum is quite similar to the trimethylamine on a clean pt surface.

As discussed before, if the hypothesis is true, trimethylamine decomposition reaction should occur if the trimethylamine is dosed before the CO dosage.The reaction does occur demonstrated by the growth of the 565 cm^{-1} peak at 25 ^{o}C. Additionally, we notice that as the trimethylamine decomposes and leaves the surface, the CO stretching frequency did not restored to 2020cm^{-1}, as observed from the previous experiment. This means that the top sites may be still occupied by the trimethylamine decomposition product.

4 **Conclusions:**

1. Trimethylamine is weakly adsorbed on Pt(111) surface. The adsorption occurs on the top site.

2. Some of the initially adsorbed trimethylamine on the clean Pt(111) dissociate to yield CN triple bonded moieties

3. The thermal desorption of trimethylamine/Pt(111) yields H_2, HCN and parent $(CH_3)_3N$.

4. Trimethylamine on Pt(111) surface HREEL spectra has been assigned.

5. Intermediate surface species have been identified by temperature dependent HREEL spectra.

6. The coadsorption of trimethylamine on CO/Pt(111) surface lowers the CO stretching by $40cm^{-1}$.

7. As indicated by our coadsorption experiments, trimethylamine and CO both bond to Pt in an on-top geometry. It appears that CO and trimethylamine do not displace one another from the on-top site. Thus the order of adsorption results in major changes in the coadsorption experiments.

Acknowledgments

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Figure captions

Fig. 1, Temperature programmed desorption of trimethylamine adsorbed on Pt(111) at 160 K. Only H_2, HCN and $(CH_3)_3N$ desorb from the surface. The mass peak at 30 (*m/e*) is a major fragment of trimethylamine. The heating rate was 5 K s^{-1}.

Fig. 2. The carbon(272eV) / platinum(237eV) Auger ratio versus trimethylamine dosage. solid and open diamonds are separate runs. Solid triangles are the carbon(272eV) / platinum(237eV) Auger ratio after TPD experiment.

Fig. 3, The carbon(272eV) / platinum(237eV) Auger ratio versus temperature at trimethylamine dosage of 600 seconds

Fig. 4, Here is the HREELS spectra taken on and off specular angle. the x axis is the energy loss in wavenumber, and y-axis is the counting rate. The counting rate for elastic scattered electron is 3.3 ten to the 4th counts per second. The full-wave at half maximum is about 40 wavenumber. The loss peaks is only a small fraction of the elastic peak, the right side y-axis is the counting rate for the loss peaks. In order to assign this spectrum, we need to look at the gas phase trimethylamine spectrum.

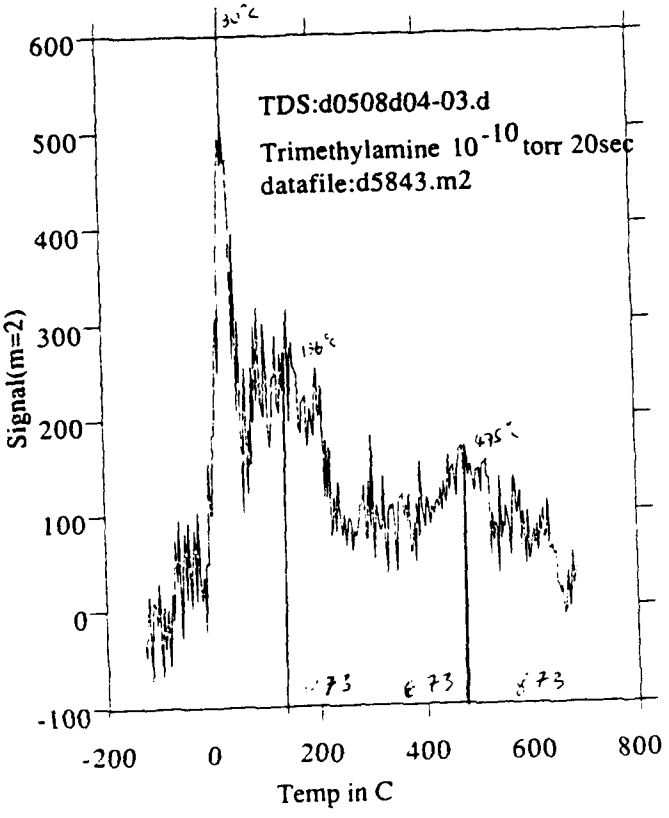
Fig. 5, On specular HREELS spectra as function of coverage.

Fig. 6, On specular HREELS spectra as function of temperature.

Fig. 7, On and off specular HREELS spectra of trimethylamine at 40 ^{o}C.

Fig. 8, On specular HREELS spectra of trimethylamine and CO with CO dosed first. HREELS spectra as function of temperature are also shown.

Fig. 9, On specular HREELS spectra of trimethylamine and CO with trimethylamine dosed first. HREELS spectra as function of temperature are also shown.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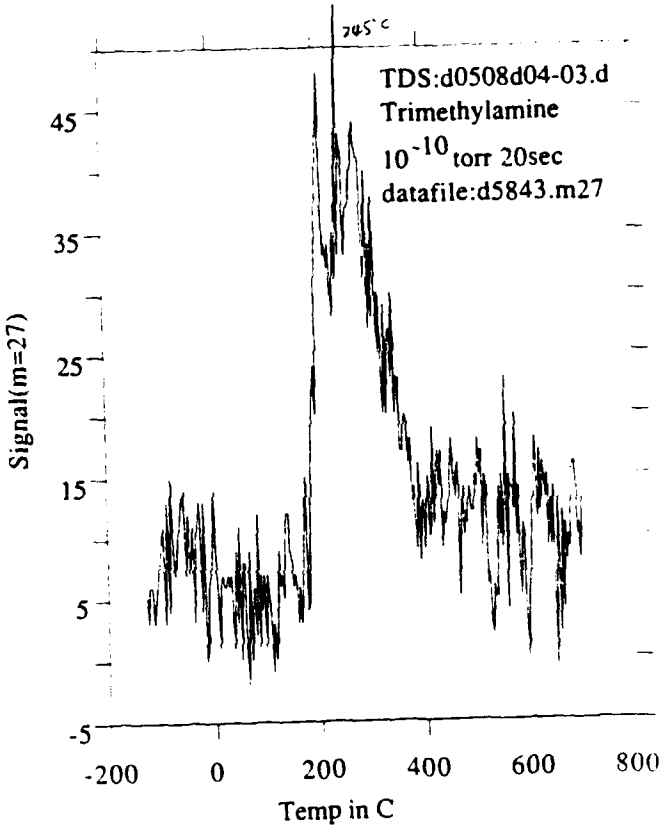
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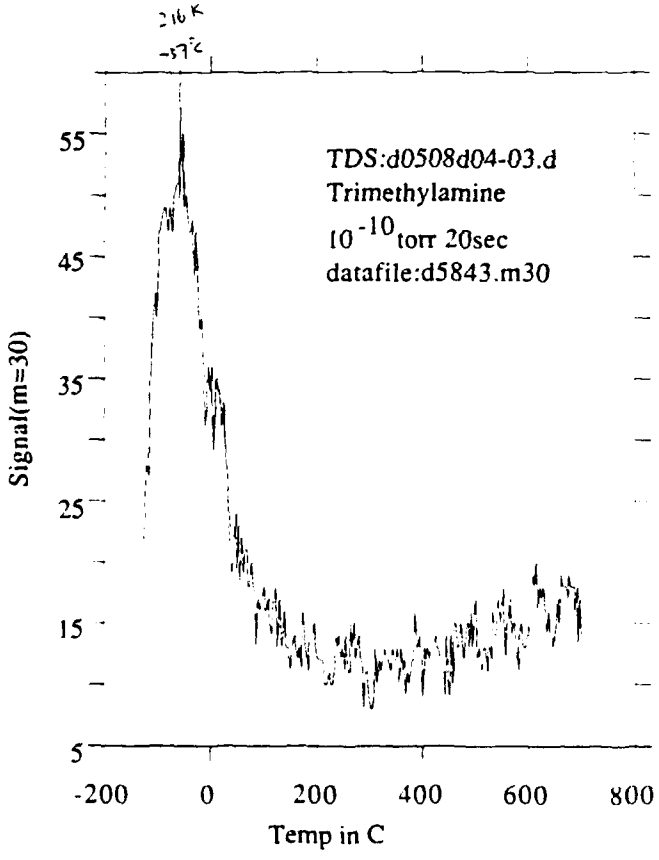
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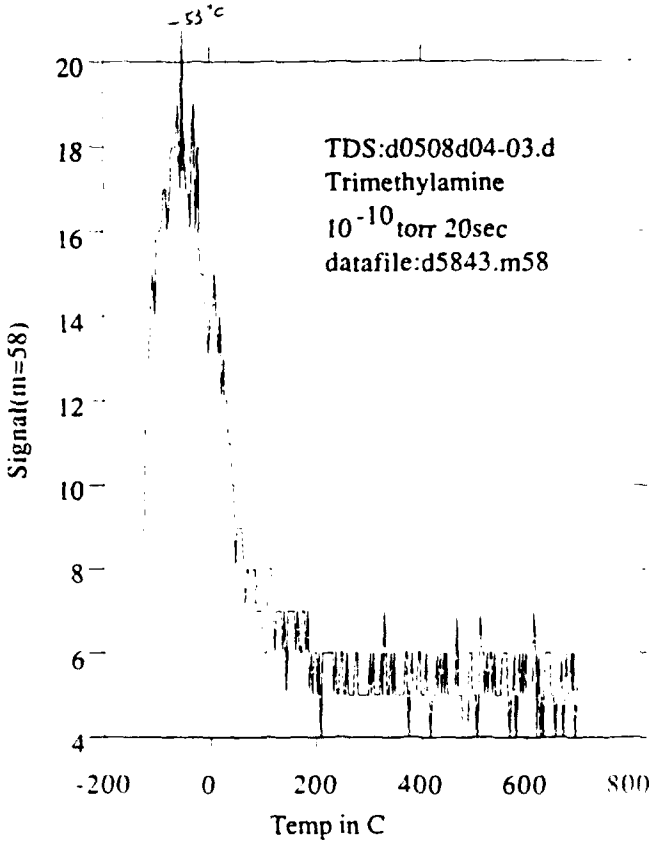
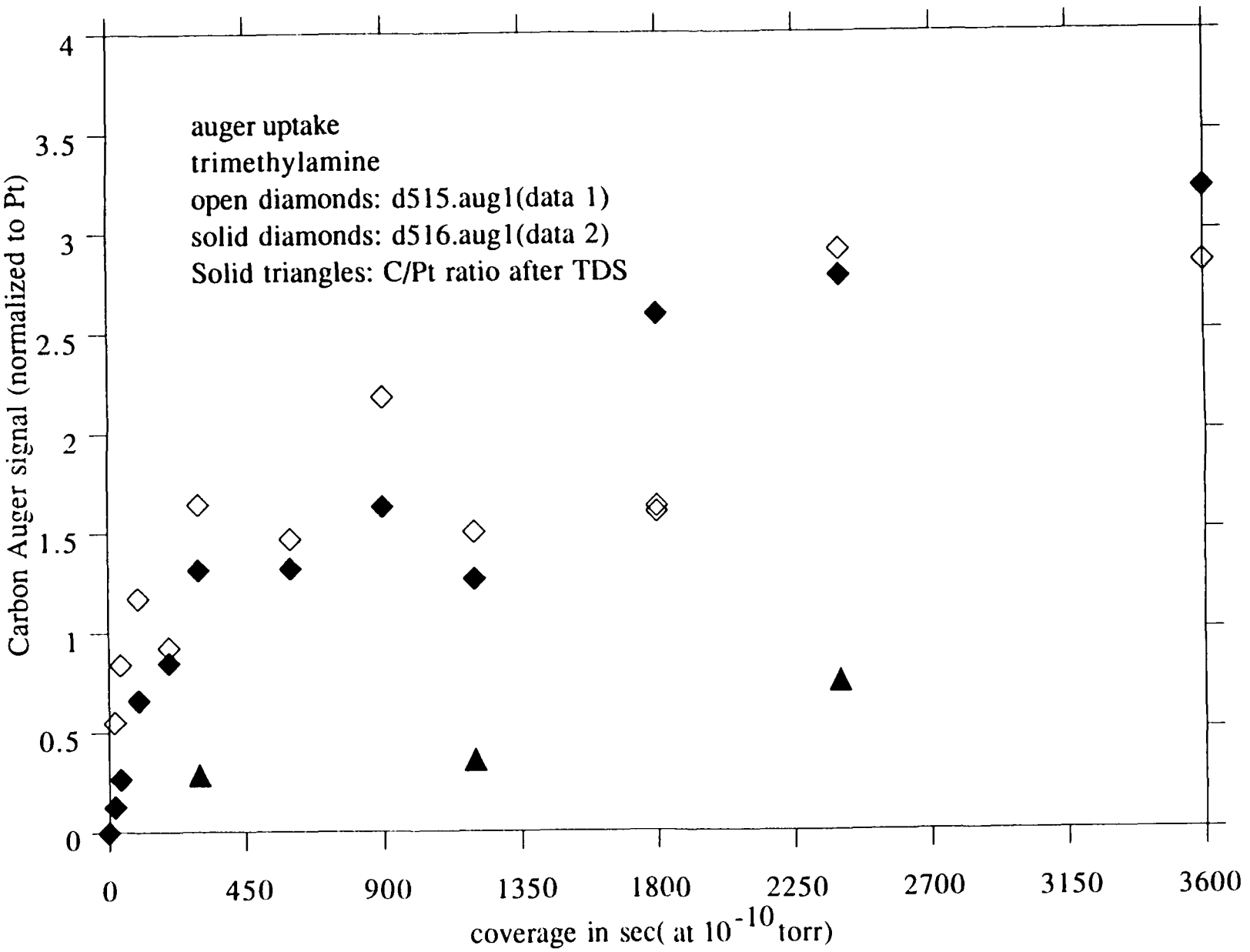
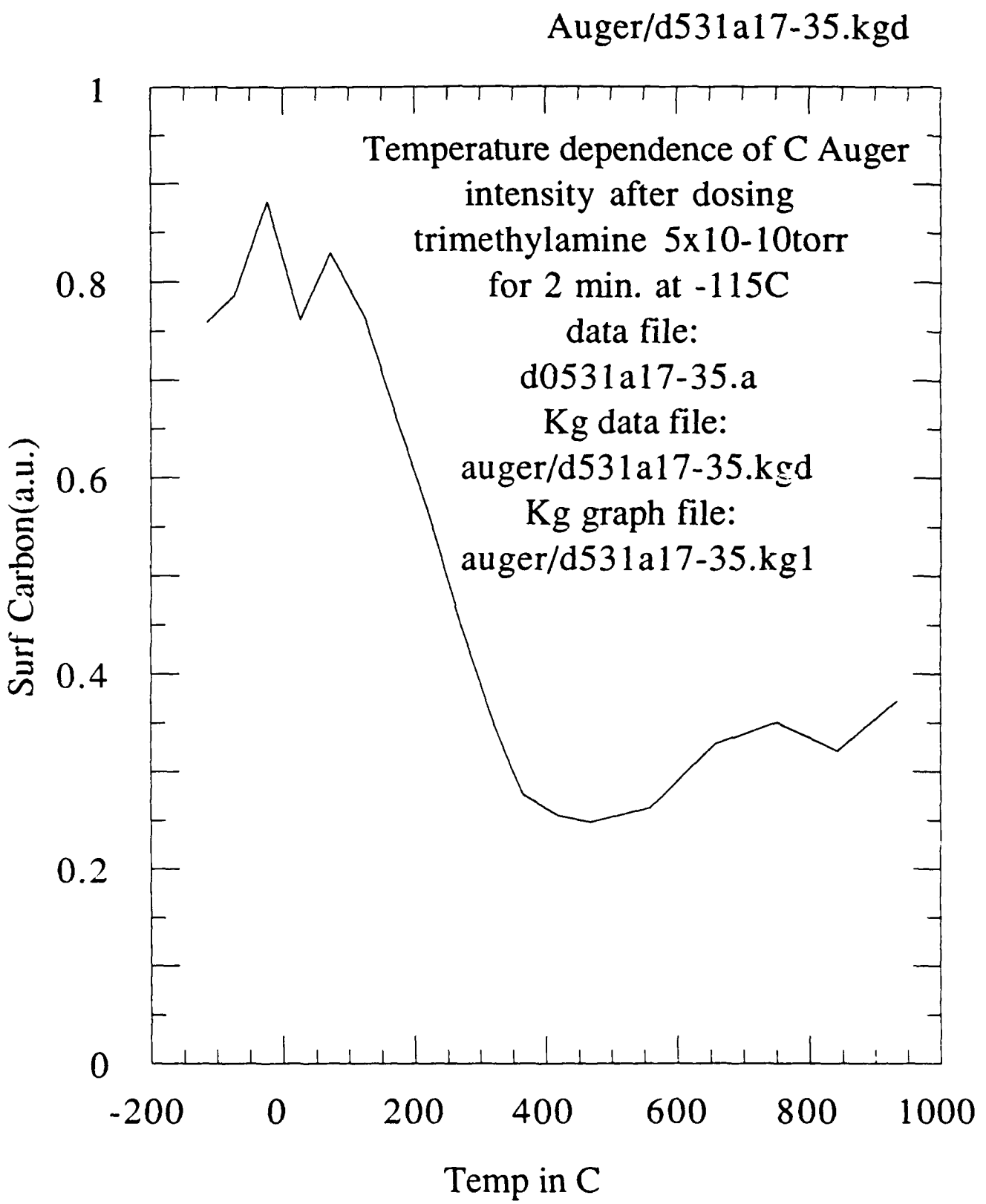
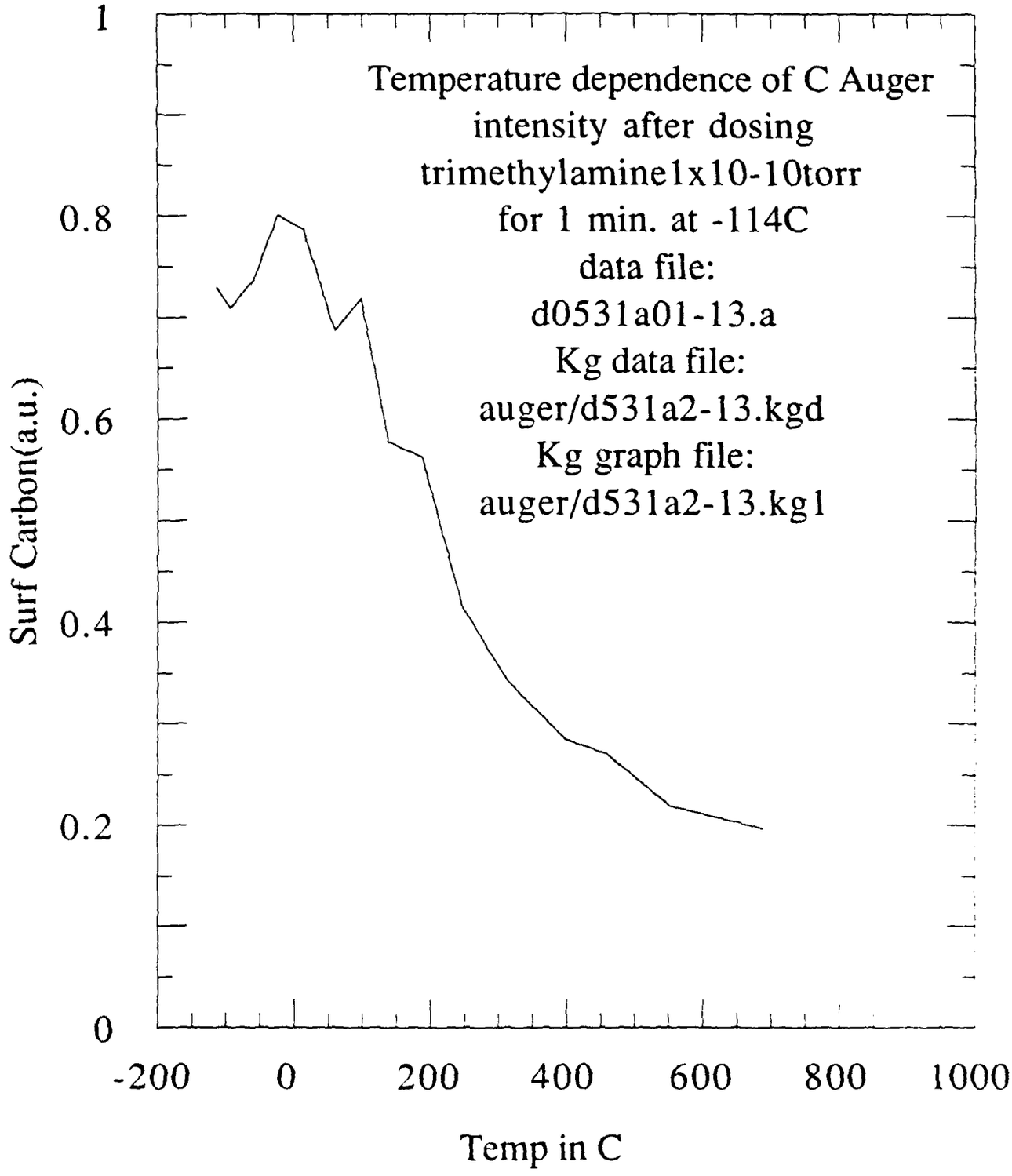
Signal(m=30)
Temp in C

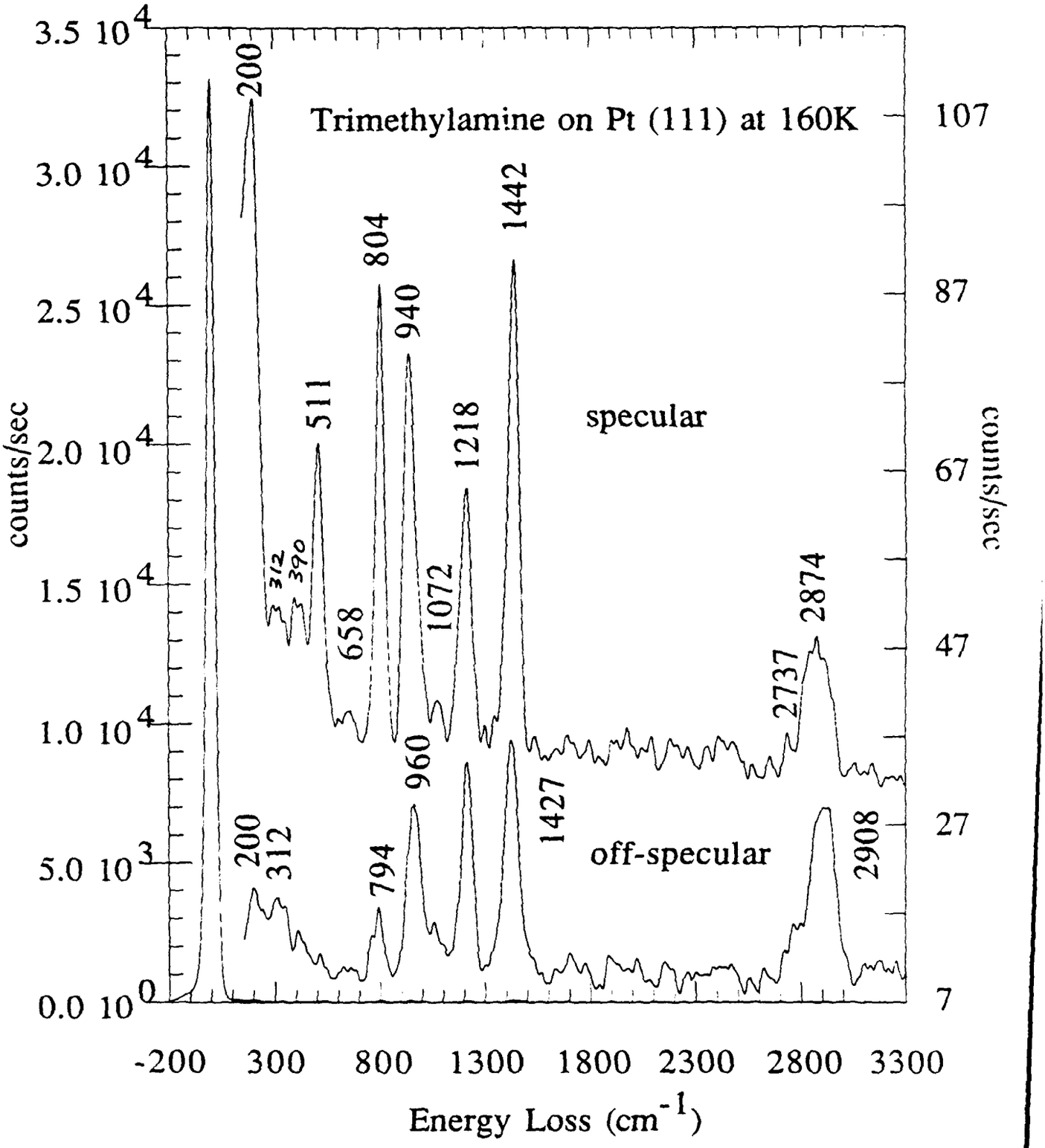

TDS:d0508d04-03.d
Trimethylamine
10^-10 torr 20sec
datafile:d5843.m58
Signal(m=58)
Temp in C

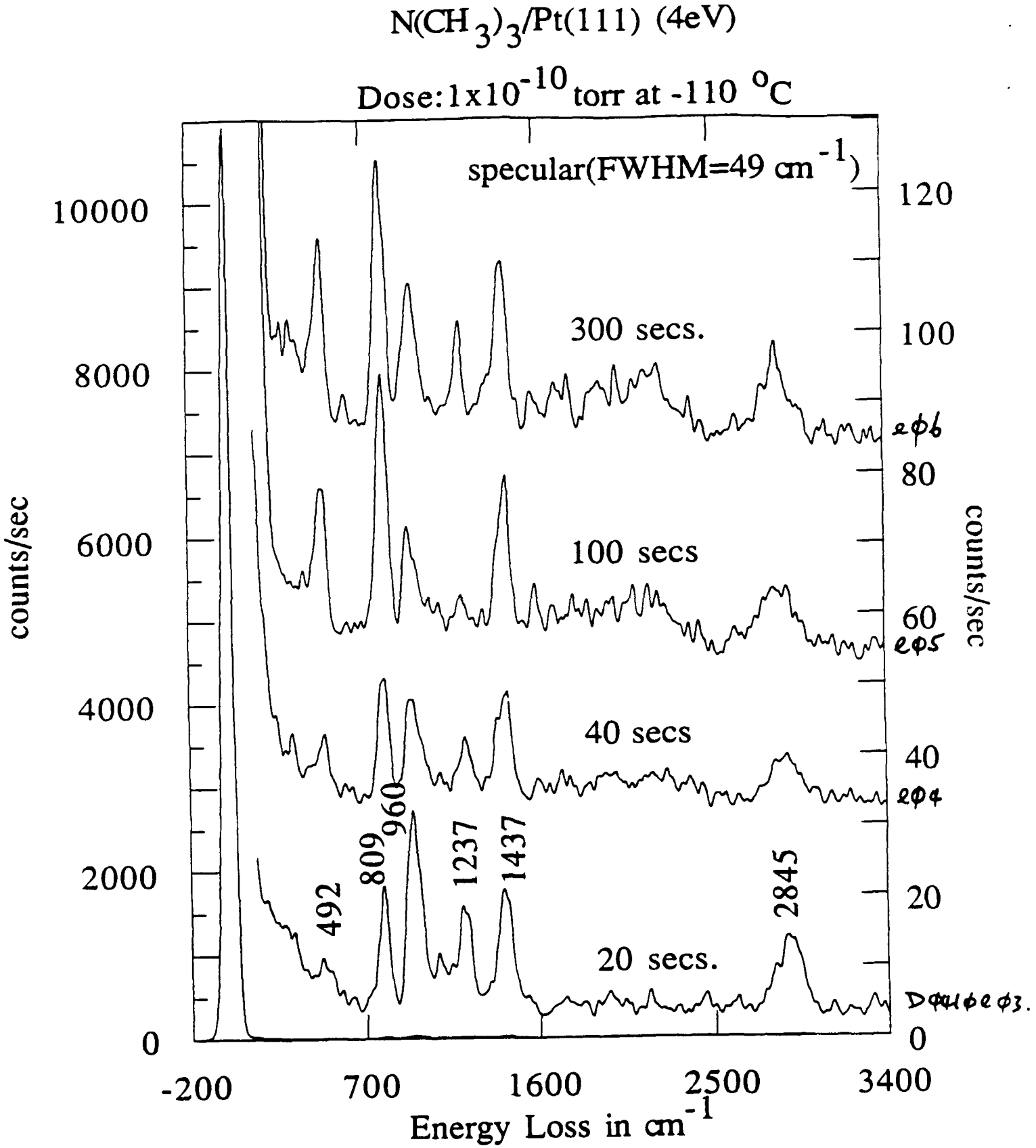

auger uptake
trimethylamine
open diamonds: d515.aug1(data 1)
solid diamonds: d516.aug1(data 2)
Solid triangles: C/Pt ratio after TDS
Carbon Auger signal (normalized to Pt)
0
0.5
1
1.5
2
2.5
3
3.5
4
0
450
900
1350
1800
2250
2700
3150
3600
coverage in sec(at 10^{-10} torr)


Auger/d531a17-35.kgd
Temperature dependence of C Auger intensity after dosing trimethylamine 5x10-10torr for 2 min. at -115C
data file:
d0531a17-35.a
Kg data file:
auger/d531a17-35.kgd
Kg graph file:
auger/d531a17-35.kg1
Surf Carbon(a.u.)
1
0.8
0.6
0.4
0.2
0
-200
0
200
400
600
800
1000
Temp in C

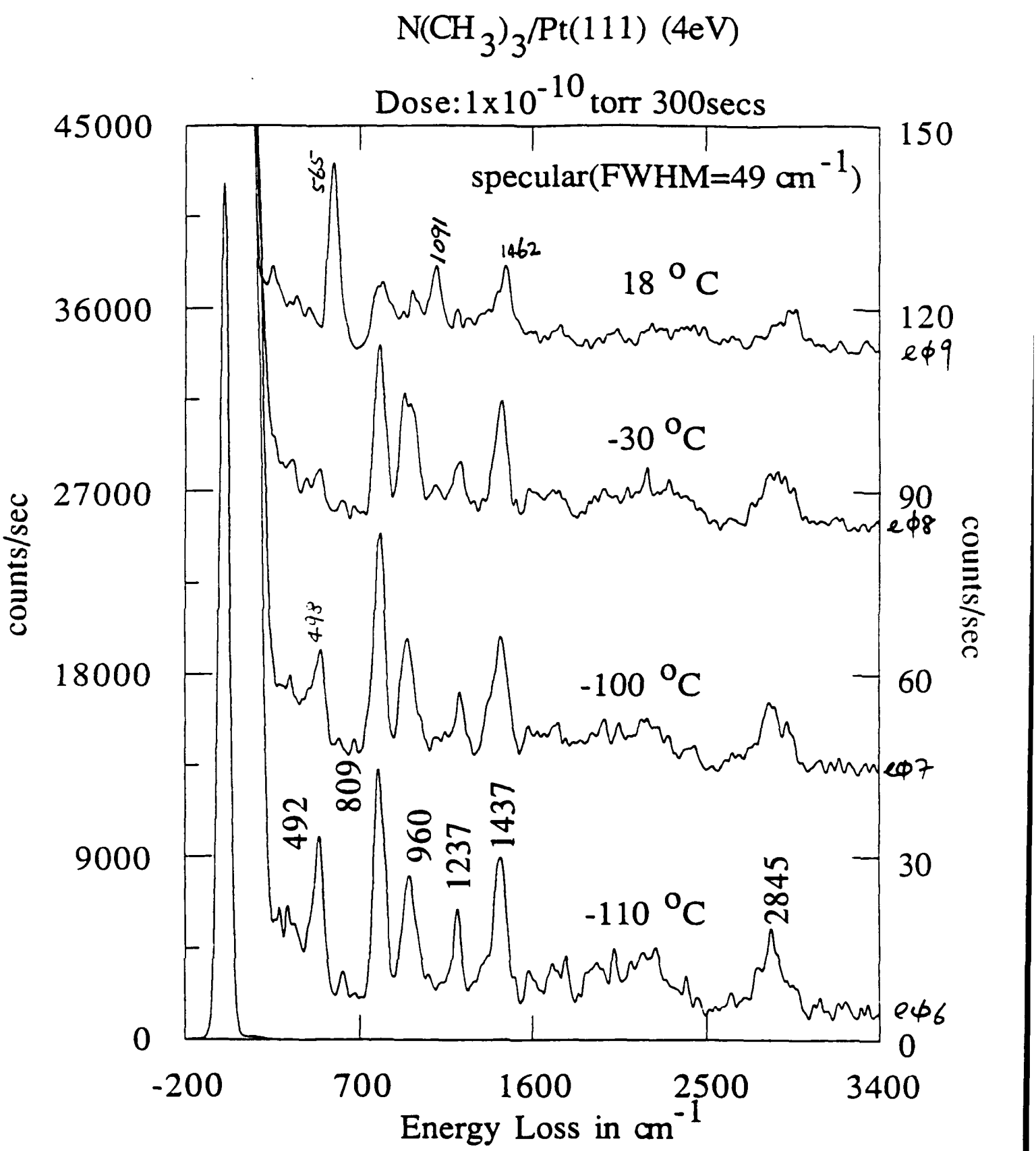
Auger/d531a2-13.kgd



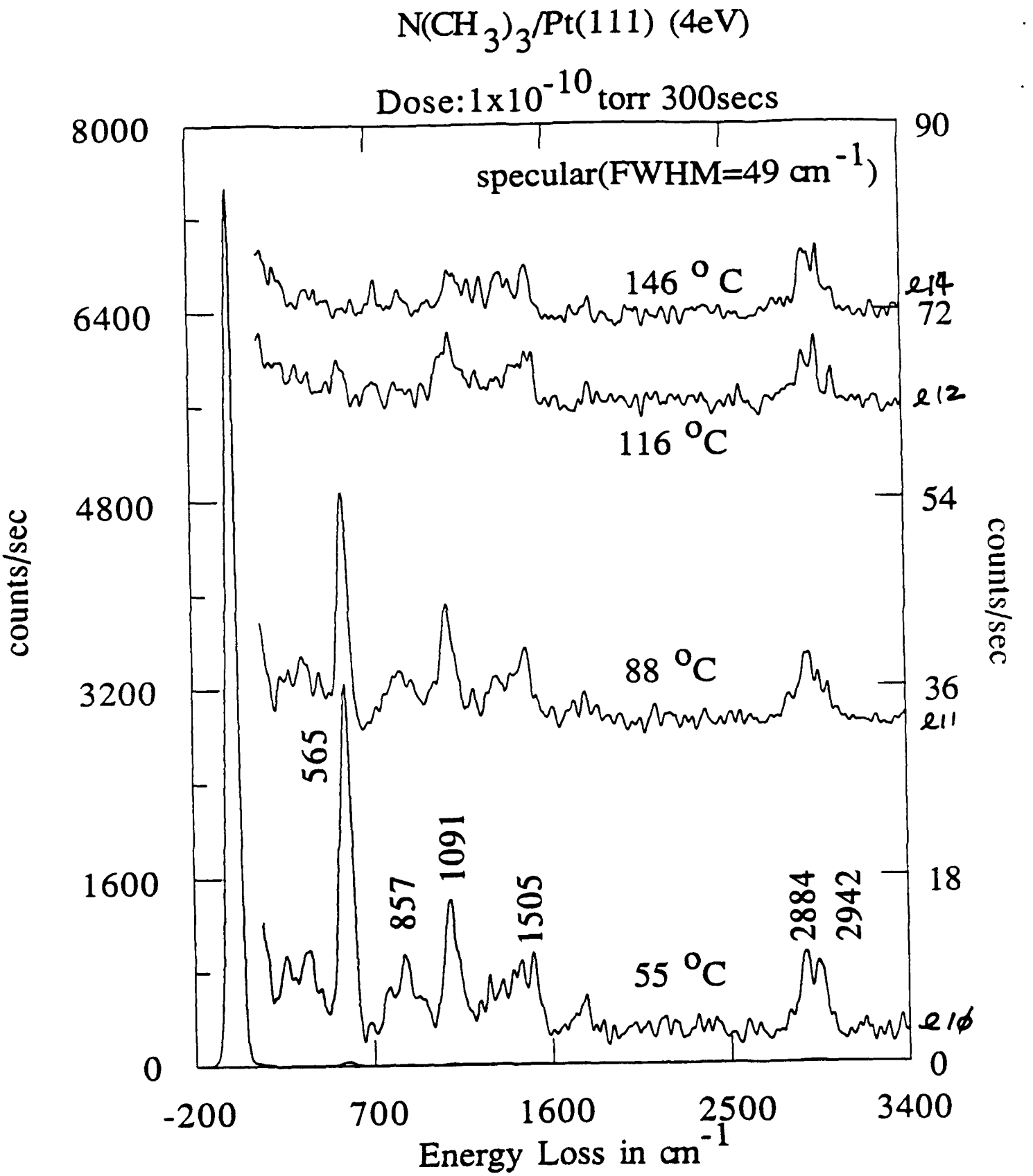

Trimethylamine on Pt (111) at 160K
specular
off-specular
counts/sec
counts/sec
Energy Loss (cm-1)
3.5 10^4
3.0 10^4
2.5 10^4
2.0 10^4
1.5 10^4
1.0 10^4
5.0 10^3
0.0 10^0
107
87
67
47
27
7
-200
300
800
1300
1800
2300
2800
3300
200
312
390
511
658
794
804
940
960
1072
1218
1427
1442
2737
2874
2908

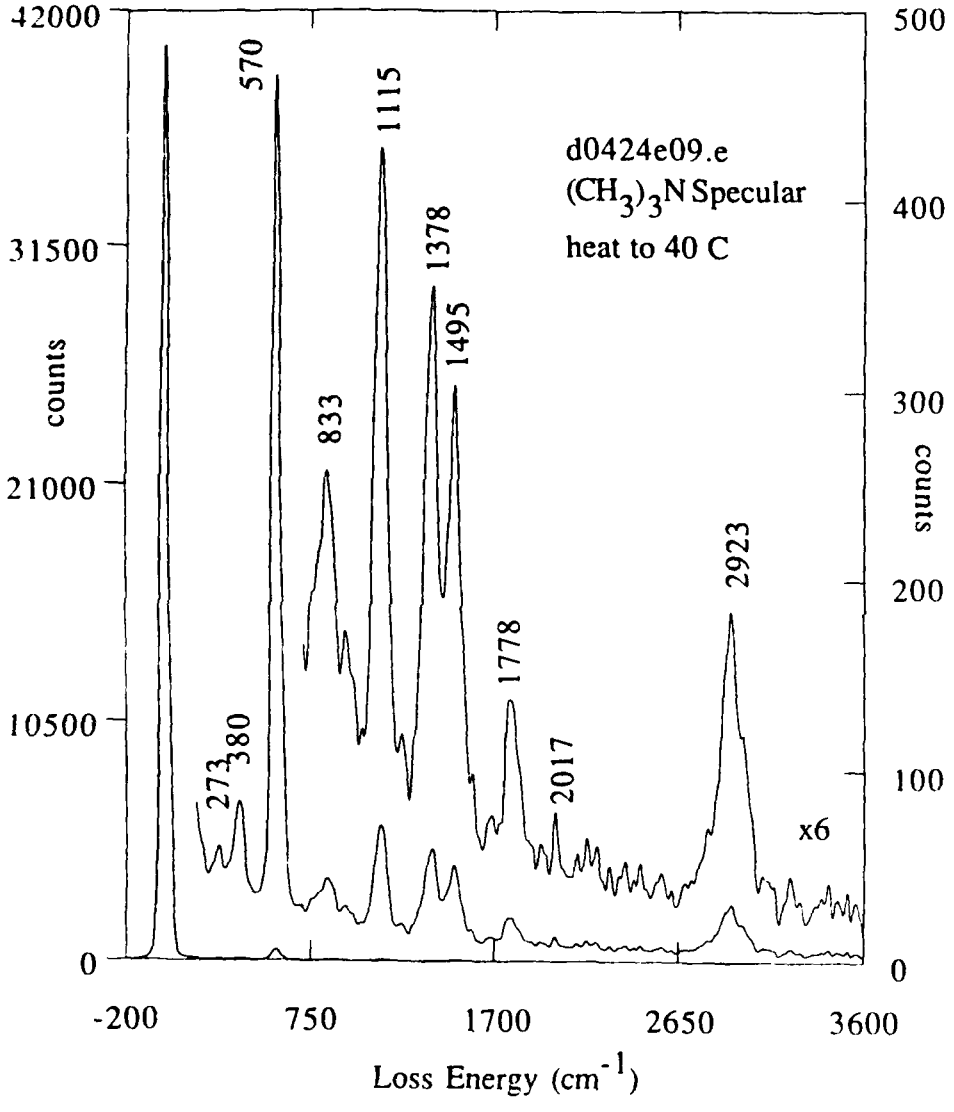

N(CH3)3/Pt(111) (4eV)
Dose: 1x10-10 torr at -110 °C
specular(FWHM=49 cm-1)
300 secs.
100 secs
40 secs
20 secs.
492
809
960
1237
1437
2845
counts/sec
counts/sec
Energy Loss in cm-1
10000
8000
6000
4000
2000
0
120
100
80
60
40
20
0
-200
700
1600
2500
3400

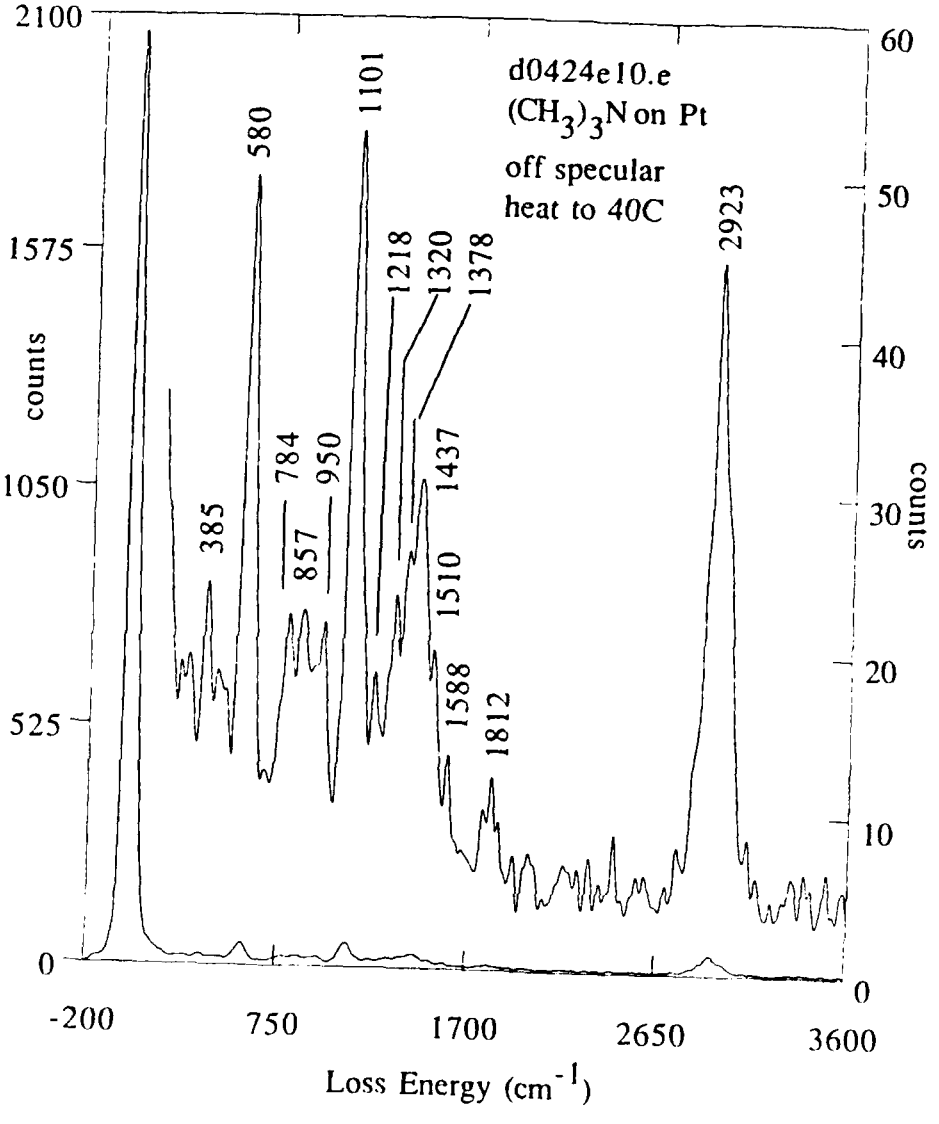
TMA(35)

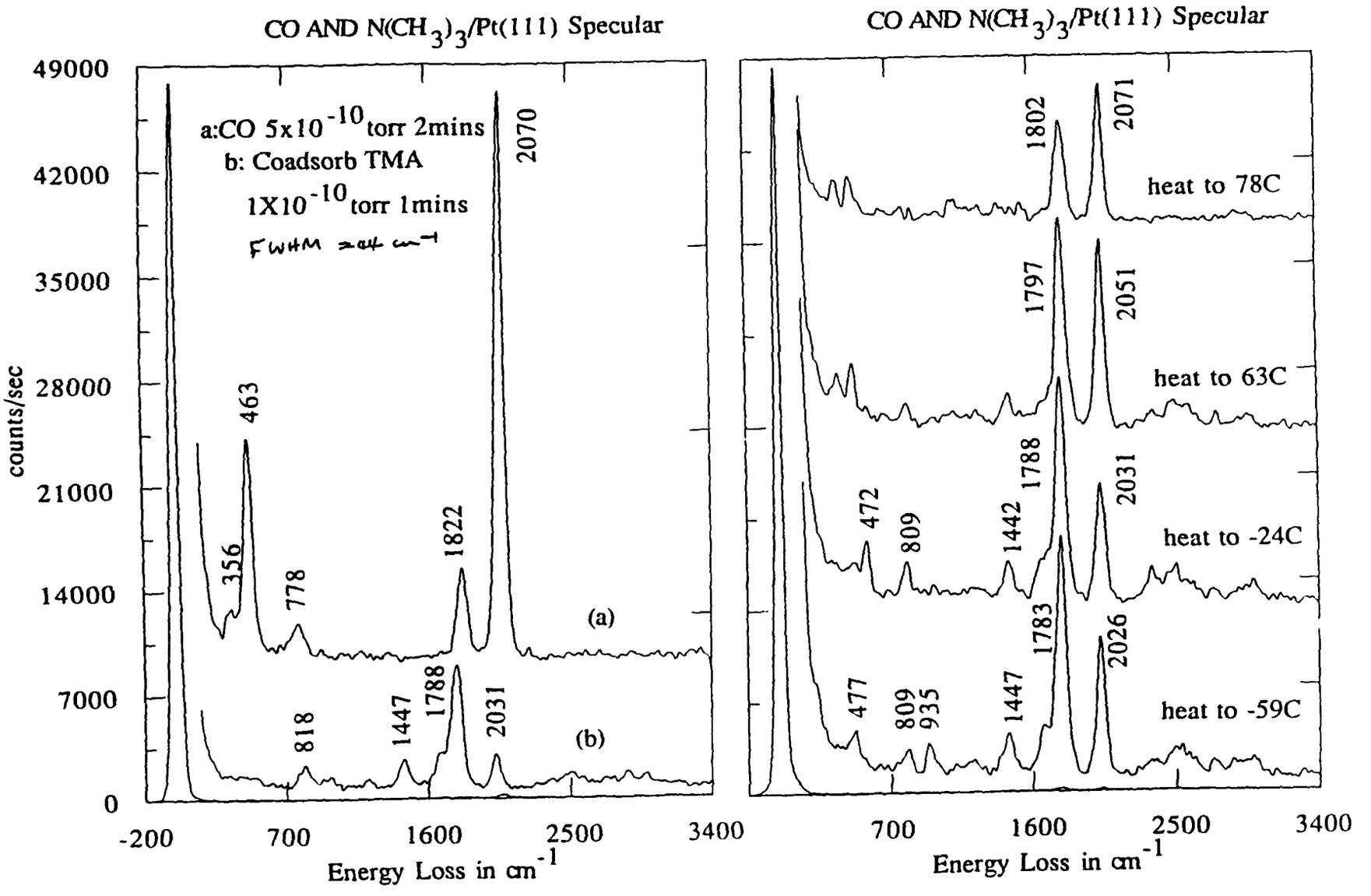

N(CH3)3/Pt(111) (4eV)
Dose:1x10-10 torr 300secs
specular(FWHM=49 cm-1)
18 °C
-30 °C
-100 °C
-110 °C
565
1091
1462
493
492
809
960
1237
1437
2845
45000
36000
27000
18000
9000
0
150
120
90
60
30
0
eφ9
eφ8
eφ7
eφ6
counts/sec
counts/sec
-200
700
1600
2500
3400
Energy Loss in cm-1

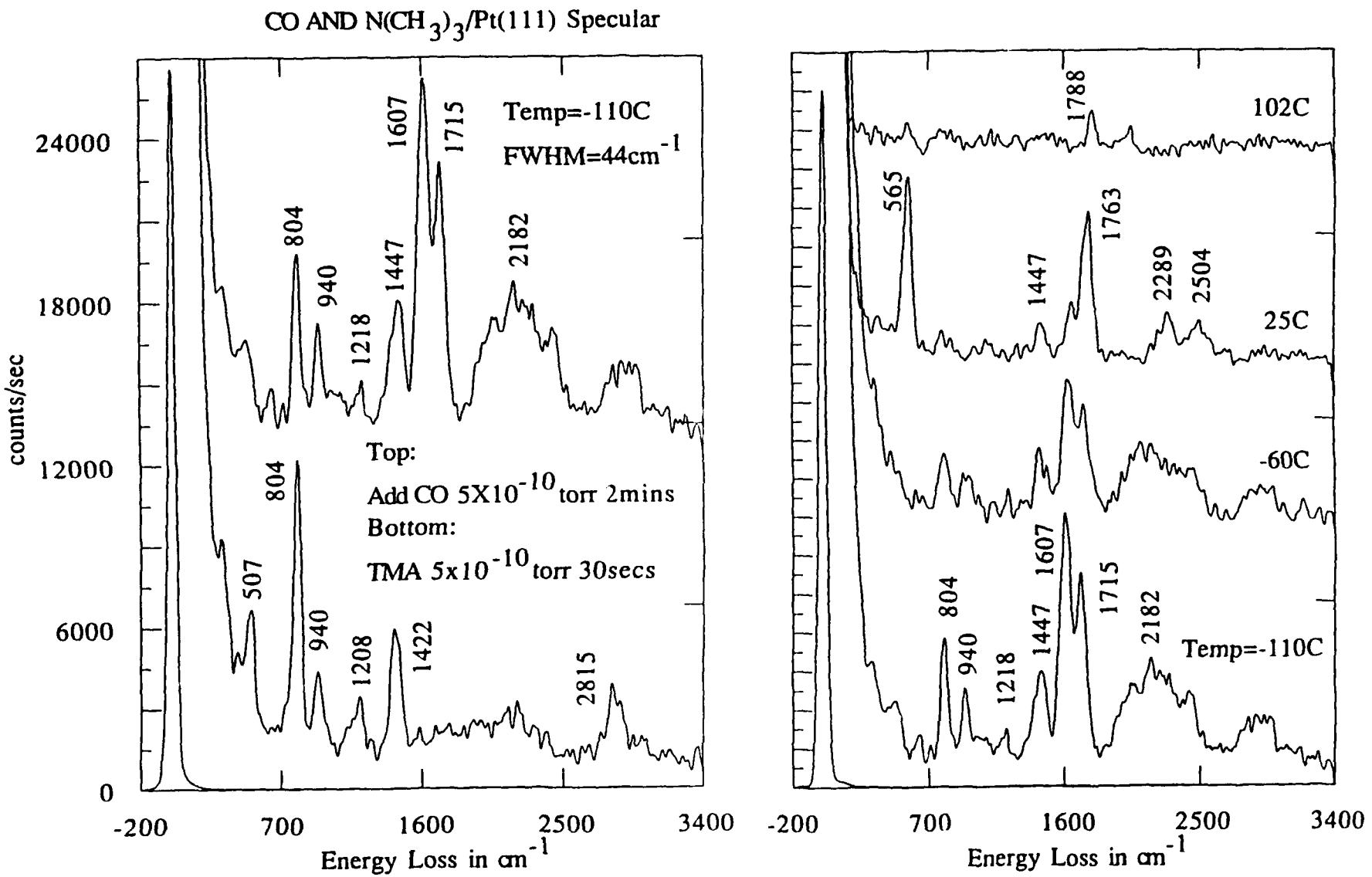
TMA (6)


N(CH3)3/Pt(111) (4eV)
Dose:1x10-10 torr 300secs
specular(FWHM=49 cm-1)
146 °C
116 °C
88 °C
55 °C
565
857
1091
1505
2884
2942
8000
6400
4800
3200
1600
0
90
72
54
36
18
0
counts/sec
counts/sec
-200
700
1600
2500
3400
Energy Loss in cm-1


d0424e09.e
$(CH_3)_3N$ Specular
heat to 40 C
counts
counts
Loss Energy (cm^{-1})
42000
31500
21000
10500
0
500
400
300
200
100
0
-200
750
1700
2650
3600
273
380
570
833
1115
1378
1495
1778
2017
2923
x6


d0424e10.e
$(CH_3)_3N$ on Pt
off specular
heat to 40C
counts
counts
Loss Energy (cm^{-1})
2100
1575
1050
525
0
60
50
40
30
20
10
0
-200
750
1700
2650
3600
385
580
784
857
950
1101
1218
1320
1378
1437
1510
1588
1812
2923


CO AND N(CH3)3/Pt(111) Specular
a:CO 5x10-10torr 2mins
b: Coadsorb TMA
1X10-10torr 1mins
FWHM = 4 cm-1
counts/sec
Energy Loss in cm-1
463
356
778
1822
2070
818
1447
1788
2031
(a)
(b)
CO AND N(CH3)3/Pt(111) Specular
1802
2071
heat to 78C
1797
2051
heat to 63C
472
809
1442
1788
2031
heat to -24C
477
809
935
1447
1783
2026
heat to -59C
Energy Loss in cm-1


CO AND N(CH3)3/Pt(111) Specular
counts/sec
24000
18000
12000
6000
0
-200
700
1600
2500
3400
Energy Loss in cm-1
Temp=-110C
FWHM=44cm-1
804
940
1218
1447
1607
1715
2182
Top:
Add CO 5X10-10 torr 2mins
Bottom:
TMA 5x10-10 torr 30secs
507
804
940
1208
1422
2815
102C
1788
565
1447
1763
2289
2504
25C
-60C
804
940
1218
1447
1607
1715
2182
Temp=-110C

$(CH_3)_3N$ Decomposition Mechanism

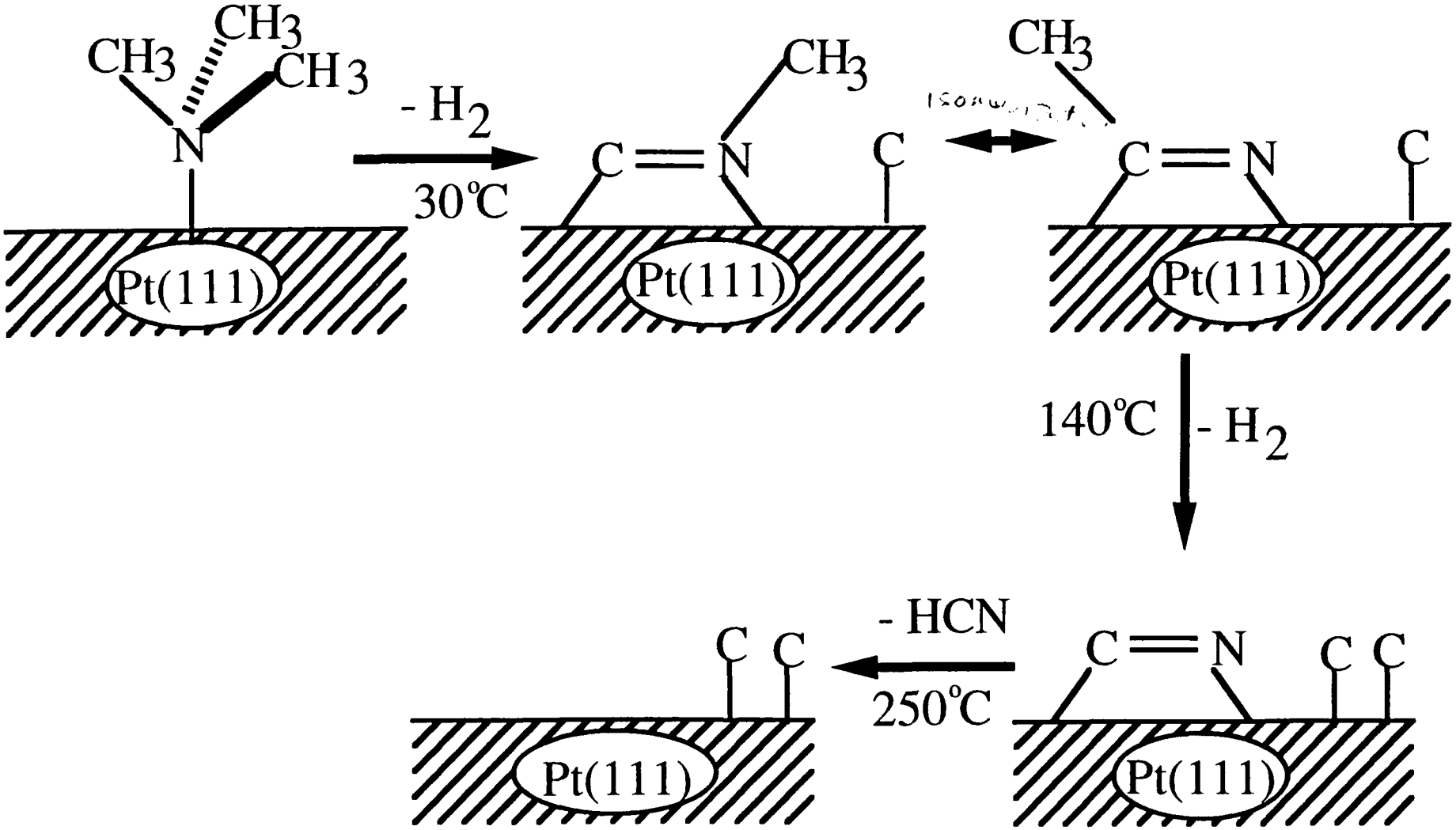


Table 1. Summary of TDS study of Trimethylamine

	Stair[1] Mo(100)	Friend[2] W(100)	Present study Pt(111)
H_2	Very small	Observed 0 °C and150 C	Observed 30 and150 °C
CH_4	Observed 180 °C	observed 150 °C	Not observed
HCN	Observed 230 °C	Not observed	Observed 250 °C
N_2	Observed 180, 600, 850 °C	observed 900 °C	Not observed at temp<700 °C
$(CH_3)_3N$	Not Observed	observed -120, -50, 40, 200 °C	observed -50 °C

1. B. W. Walker and P. C. Stair, Suf. Sci. 103, 315 (1981).

2. K. A. Pearlstine and C. M. Friend, J. Am. Chem. Soc., 108,5837 (1986) and 108, 5842 (1986).

Table 2. Summary of Trimethylamine HREEL Spectra Assignments

Assignments	$(CH_3)_3N$ (gas) Ref.1	$(CH_3)_3N$ (gas) compressed	$PtBr_2(NMe_3)_2$ Ref.2	HREELS
CH_3 Torsion	ν_{22}=269,ν_{11}=261	261-269		
NC_3 Rock	---	---	254	200
NC_3. Def.	ν_7=366	366	304	312
NC_3 Def.	ν_{21}=423	423	---	390
Pt---N stretch	---	---	556	511
NC_3 Sym. Stre.	ν_6=825	825	816	804
NC_3 Asym. Str.	ν_{20}=1043	1043	968	940
CH_3 Wag	ν_{19}=1102	1102	---	1072
CH_3 Rock	ν_5=1183	1183	---	1218
CH_3 Rock	ν_{18}=1273,ν_{10}=1320	1273-1320	---	1250
CH_3 Deform	ν_3=1466,ν_4=1453 ν_9=1460,ν_{15}=1478 ν_{16}=1459,ν_{17}=1444	1444-1478	---	1442
C-H Stretch	ν_1=2950,ν_2=2872 ν_8=2970,ν_{12}=2978 ν_{13}=2822,ν_{14}=2774	2774-2978	---	2874

Ref. 1 a) J. N. Gayles, Spetrochimica Acta, 23A, 1521 (1967). b) J. R. Barelo and J. Bellanato, Spectrochimica Acta, 8, 27 (1956).

Ref. 2 a) P. L. Goggin, R. J. Goodfellow and F. J. S. Reed, J. C. S. Dalton, (1972) 1298 b) P. L. Goggin, R. J. Goodfellow, S. R. Haddock, J. R. Knight, F. J. S. Reed and B. F. Taylor, J. C. S. Dalton, (1973) 523

Table 3 Assignments of HREEL spectra of trimethylamine on Pt(111) after annealed to 40°C

Assignments	CH_3CN/Pt(111) Avery et al[12]	$(CH_3)_3N$/Pt at 40 °C
Pt-$CNCH_3$ stretch	280	273
Pt-$CNCH_3$ asym. str.	410	380
CCN bend	605	570
C-C stretch	920	833
CH_3 rock	1060	1115
CH_3 sym.bend	1375	1378
CH_3 deg.bend	1435	1495
C=N Stretch	1615	1778
C-H Stretch	2960	2923